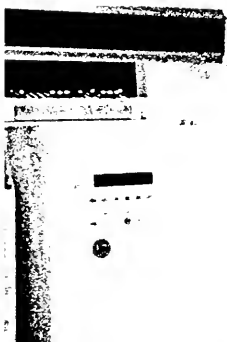
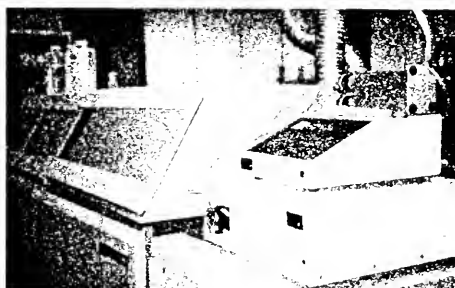
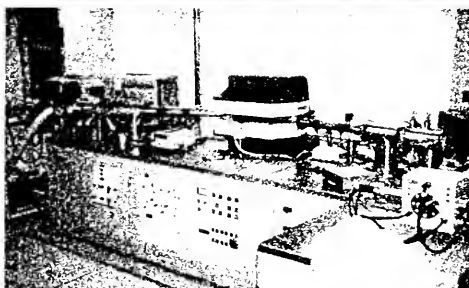


1996 Annual Report

RESEARCH AND DEVELOPMENT



**Analytical Laboratory Services
Ontario Ministry of Environment & Energy**

April, 1997

 **Ontario**

1996 Annual Report
Research and Development
Analytical Laboratory Services
April 1997

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Overview

Since the previous report in this series, the Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE) has made substantial progress in its evolution away from high-volume, routine testing and towards core functions and reference centre activities. Although Research and Development is not the principal focus of LSB, some development work is critical to ensure our MOEE customers are equipped with the appropriate tools to investigate complex environmental issues.

Substantial progress was made in several areas of method development in 1996. In addition to bringing on-line new methods for environmental contaminants, it was more important than ever to improve the sample throughput and cost effectiveness of methods. As usual, LSB customers provided the principal driving force for R&D studies.

For further information on any of the projects described in this report, readers are directed to the Study Leader, or to the Author:

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New Applications of Technology

Introduction

The use of sophisticated instrumentation is a common feature of many of the projects in this section, in which the projects are ones where the specific application depends more on the technology used than other aspects of the methodology. Projects utilizing gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), and Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) are described. A relatively new type of mass spectrometer, the ion trap, has been evaluated for use in the determination of selected compound classes. Work is also ongoing to develop methods based on sample preparation using solid-phase extraction (SPE). In SPE methods that have been developed, LSB staff have virtually eliminated the use of toxic solvents previously used for sample extraction.

Of the new technologies investigated, applications of SPE sample preparation and of the ion trap mass spectrometer show considerable promise for widespread application, because of the relatively low cost of these technologies, and their excellent performance demonstrated by LSB staff and others. LC-MS is not yet in widespread use, but improved sensitivity in recent interface designs, and the recent availability of lower cost bench-top models may lead to rapid growth in the applicability of this technology to environmental analysis. Although ICP/MS is already established as one of the most important technologies for environmental metals trace determinations, addition of HPLC and direct insertion nebulization (DIN) to the front-end greatly increases the importance of ICP/MS for the determination of environmentally important organometallic compounds.

I. Determination of Diquat and Paraquat by Liquid Chromatography-Mass Spectrometry

| | |
|---------------|---|
| Study Leader: | Vince Taguchi |
| Study Team: | Steve Jenkins, Dave Wang, Patrick Crozier |
| Customer: | Drinking Water Surveillance Program Clients, MOEE Regional Offices |

Objective

To develop a simple, rapid and selective method for the determination of diquat and paraquat in water samples.

Background

US EPA method 549.1 for diquat and paraquat utilizes an ion-pairing technique for isolating these compounds on an SPE cartridge or Empore disk followed by ion-pair liquid chromatography and UV detection. Other documented SPE methods use non-volatile buffers and strong inorganic acids (HCl) for cartridge elution. The methods are very cumbersome and some do not work very well on real samples.

Therefore, development began on a method employing a simpler sample preparation procedure combined with the selectivity of Electrospray Ionization Mass Spectrometry (ESI-MS). However, the non-volatile ion-pairing reagents and non-volatile buffers used for LC-UV analyses are incompatible with ESI. Also, HCl is not compatible with "316" stainless steel in LC systems.

Results

Diquat and paraquat were isolated on C-2, C-4, C-8, C-18 and CN Solid Phase Extraction (SPE) cartridges and eluted with a trifluoroacetic acid (TFA) solution. The chromatography was developed on a C-1 column (15 cm x 1 mm i.d.) using TFA (or HFBA), methanol (or acetonitrile) and water as mobile phase. Because the TFA (or HFBA) used to obtain good chromatography also suppresses ionization of analytes in the ESI source, a mixture of propionic acid (or butyric acid) and isopropanol was added post column to counteract this suppression. Mass spectrometry was performed at low resolution (1,000) to be compatible with single quadrupole and ion trap MS. Quantitation is accomplished by isotope dilution with d_4 -diquat and d_6 -paraquat.

Current Status

Some interference problems with the proposed method need to be resolved. Performance data have to be obtained to validate the method. Experiments thus far indicate that detection limits in the low $\mu\text{g/L}$ range are achievable. This should be sufficient to meet the Ontario Drinking Water Objectives of 70 $\mu\text{g/L}$ for diquat and 10 $\mu\text{g/L}$ for paraquat.

II. Speciation of Aluminum in Drinking Water by HPLC/DIN/ICP/MS

| | |
|---------------|---|
| Study Leader: | Mark Powell |
| Study Team: | Daniel Wiederin (Cetac Technologies) |
| Customer: | Wastewater Technology Section (Heather Broomer) |

Objectives

To investigate the complex chemistry of aluminum to find a relationship between soluble and insoluble aluminum species and to develop a method to measure "free" ionic aluminum.

Background

Presently, there are concerns with negative human health effects from aluminum in drinking water. Although there are many conflicting reports in the literature, measurement of "free residual" aluminum has been requested in addition to the established method for "total" aluminum determination. The customer has established a desire to find a relationship between soluble and insoluble aluminum under different water quality conditions (ie; pH, alkalinity, TOC, etc.).

An analytical technique based on separation by ion chromatography using a micro-column developed by Cetac Technologies and designed for ionic speciation of aluminum is being investigated. As the detection system used is DIN/ICP/MS, the technique is selective and sensitive enough to monitor total ionic and speciated ionic aluminum at concentrations below typical drinking water levels.

Results

Initial results indicate that an ionic aluminum chromatogram can be produced from the micro-column. Total aluminum was also determined in the same measurement. The retention time of the signal is consistent - leading to a possibility of quantitative measurements. The detection limit is currently estimated to be in the ppb range.

Current Status

A joint study with Health and Welfare Canada (H&W) was conducted in the summer of 1996. A method using LC columns to separate "dissolved" and "undissolved" aluminum has been developed at their laboratory and a parallel study was run in conjunction with the MOEE-LSB Spectroscopy Unit. MOEE laboratory staff set up a study site at Lakeview Water Treatment Plant and collected split samples of raw and treated water. These samples were analyzed at both H&W and LSB laboratories and the data are being analyzed.

The analytical capability of the HPLC/DIN/ICP-MS technique for quantification of aluminum species in drinking water was not investigated in 1996. Further development work in this area is planned for late 1997.

Future work to compare the LSB HPLC/DIN/ICP-MS method to the H&W LC/ICP-MS method is planned.

III. SPME for Trace PAH in Waste and Drinking Water Samples

| | |
|---------------|---------------------------------------|
| Study Leader: | Walter Offenbacher |
| Study Team: | George Kanert |
| Customer: | Litigation and Waste Analysis Section |

Objectives

To assess the feasibility of using micro-fiber extraction (solid phase micro-

extraction, or SPME) for the analysis of polynuclear aromatic hydrocarbons (PAH) at trace levels in waste and drinking water samples.

Background

The extraction methods currently in use at LSB for the analysis of PAH in aqueous samples suffer from several limitations:

- ☐ liquid/liquid extraction uses large volumes of organic solvents to isolate PAH and other contaminants from aqueous samples;
- ☐ liquid/liquid extractions are labour-intensive;
- ☐ the sample concentration steps needed to achieve the required detection limits are potential significant sources of error.

The novel technique of SPME exposes a defined length of surface-coated fused silica fibre to a defined amount of aqueous sample. After a predetermined exposure time, the fibre is introduced into the heated zone of a GC injection port. Analytes are desorbed from the fibre and analyzed via conventional GC/ECD/FID or GC/MS.

Results

All analytical data were obtained using several 7 μm and 30 μm polydimethylsiloxane coated fibres with manual injector on a Varian GC and Saturn ion trap system. After determining the reproducibility of this system for the target compounds (naphthalene, acenaphthene, anthracene, chrysene, and benzo(a)pyrene) with isooctane injections containing 5.0 $\mu\text{g/L}$ of each PAH, the optimum fibre exposure time (45 minutes), and optimum fibre insertion depth (4 cm), were determined.

In these initial tests, the reproducibilities (4 replicate determinations) for the PAH examined ranged from 8-58% relative standard deviation (0.25 $\mu\text{g/L}$ PAH concentrations) to 11-85% relative standard deviation (10 $\mu\text{g/L}$ PAH concentrations).

Current Status

The reproducibility of the SPME method was disappointing, but there were many experimental variables in these initial experiments, not all of which were examined fully. Future studies will concentrate on finding and reducing the major sources of determinate error.

IV. SPE GC/MS Analysis of PAH in Drinking Waters

| | |
|---------------|------------------------------------|
| Study Leader: | Patrick Crozier |
| Study Team: | L. Matchuck |
| Customer: | All Drinking/Surface Water Clients |

Objectives

To develop a solid phase extraction GC/MS-based method for the trace level testing of polynuclear aromatic hydrocarbons (PAH) in drinking waters, surface waters, and groundwaters, which will provide high quality data with faster analysis time, increased analytical capacity, and a reduction in the use of hazardous chemicals.

Background

Polynuclear aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants. Several PAH have been found to have carcinogenic properties eliciting their inclusion in environmental control legislation. The World Health Organization (WHO) has recommended the concentration of six representative PAH (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene) not to collectively exceed 200 ng/L in drinking waters. The Ontario Ministry of Environment and Energy has established the maximum acceptable concentration (MAC) for benzo(a)pyrene in drinking waters to be 10 ng/L (Ontario Drinking Water Objectives - Revised 1994).

The Drinking Water Analyses Section tests for PAH using a liquid/liquid extraction-HPLC/Fluorescence method. Sample preparation is by batch processing with external quality control (QC) measures. Although the HPLC method is reliable (CAEAL accredited), it possesses several less than ideal qualities. Its major drawbacks are the use of large quantities of hazardous solvents (extraction solvent and HPLC mobile phase), low column resolving power, restricted linear range, front end interferences with highly coloured samples, and the need to confirm positive results by mass spectrometry. The development and use of solid phase extraction GC/MS methodology eliminates most of the problems associated with the current HPLC testing method as well as permits the monitoring of individual sample processing performance through the use of labelled surrogates and internal standards.

Results

A routine SPE GC/MS method has been developed to test for 15 PAH target compounds. The wet chemical preparation procedure requires 800 mL of sample and consists of sample acidification (pH = 2), surrogate addition, sample aspiration through C₁₈ SPE cartridges, cartridge air drying, toluene elution and extract evaporation. Instrumental analysis is completed after the addition of an internal standard. Compound separations are accomplished using a 30 metre DB-5ms column and a 35 minute double ramp oven program. A six-segmented single ion monitoring (SIM) program is used to identify (retention time plus target ions), quantify (parent ion) and confirm (ion ratios) target compounds. The performance of this method is shown by the results in the following table.

| PAH SPE GC/MS Method - Instrument and Method Performance | | | | | | | | |
|--|---|------|----------------|------|------------|------|--|------|
| Target Compound | Instrument Performance (500 pg/uL, n=10) | | | | | | Method Performance (500 ng/L, n=14) | |
| | Retention Time | | Quantification | | Ion Ratio | | Recovery (%) | %RSD |
| | Result (min) | %RSD | Result (%) | %RSD | Result (%) | %RSD | | |
| phenanthrene | 10.08 | 0.01 | 102 | 3 | 23 | 1 | 96 | 9 |
| anthracene | 10.20 | 0.02 | 101 | 4 | 22 | 1 | 89 | 9 |
| fluoranthene | 12.99 | 0.01 | 102 | 3 | 19 | 1 | 92 | 11 |
| pyrene | 13.35 | 0.01 | 102 | 4 | 20 | 1 | 91 | 11 |
| benzo(a)anthracene | 16.57 | 0.01 | 104 | 3 | 26 | 1 | 76 | 12 |
| chrysene | 16.65 | 0.01 | 103 | 3 | 28 | 1 | 82 | 13 |
| dimethylbenz(a)anthracene | 19.10 | 0.01 | 102 | 3 | 63 | 1 | 68 | 18 |
| benzo(b)fluoranthene | 19.10 | 0.01 | 106 | 3 | 22 | 1 | 83 | 14 |
| benzo(k)fluoranthene | 19.16 | 0.01 | 104 | 3 | 21 | 1 | 90 | 13 |
| benzo(e)pyrene | 19.71 | 0.01 | 105 | 3 | 29 | 1 | 77 | 13 |
| benzo(a)pyrene | 19.84 | 0.01 | 106 | 3 | 22 | 1 | 76 | 16 |
| perylene | 20.02 | 0.01 | 105 | 3 | 26 | 1 | 79 | 18 |
| indeno(123-cd)pyrene | 22.93 | 0.01 | 108 | 3 | 20 | 1 | 83 | 20 |
| dibenzo(ah)anthracene | 23.05 | 0.01 | 109 | 4 | 24 | 1 | 75 | 19 |
| benzo(ghi)perylene | 23.79 | 0.01 | 94 | 4 | 20 | 3 | 76 | 21 |

Current Status

Method development is complete. The method (LSB LIMS Method # E3399A) is currently being used for routine sample testing. The SPE GC/MS method has been validated against the LSB liquid/liquid extraction HPLC/Fluorescence method using real matrix spike samples, NIST reference materials and CAEAL audit samples. The method is currently under going CAEAL accreditation.

Publications and Presentations

The Determination of Polynuclear Aromatic Hydrocarbons (PAH) in Water by Solid Phase Extraction (SPE) and Gas Chromatography - Mass Spectrometry, MOEE/LSB LIMS Method # E3399A, Drinking Water Analyses Section.

V. Evaluation of an Ion Trap Mass Spectrometer for the Analysis of Hazardous Organic Compounds

| | |
|---------------|---------------------------------------|
| Study Leader: | Patrick Crozier |
| Study Team: | Mike Sage, Gerry Ladwig , Eric Reiner |
| Customer: | All LSB Clients |

Objectives

To evaluate the capabilities of a bench-top gas chromatograph / ion trap mass spectrometer (GC/ITD) system. To develop rugged routine GC/ITD analytical methods for the testing of hazardous organic compounds in a variety of environmental matrices.

Background

Analysis of organic compounds is typically accomplished by separating the components of a complex mixture using gas chromatography (GC) or liquid chromatography (LC). The separated components can then be detected with any number of detectors based on the required selectivity and/or sensitivity. Electron capture detectors (ECD) are typically used for halogenated compounds while flame

ionization detectors (FID) are most often used for non-halogenated compounds. Over the last several years, the cost of mass spectrometers has decreased significantly and the mass spectrometer, because of its high degree of selectivity, has become a common GC and LC detector. Advanced MS modes such as high resolution mass spectrometry (HRMS) and mass spectrometry/mass spectrometry (MS/MS) are even more selective than normal MS, but are rarely used because conventional instruments are very expensive and difficult to set-up and operate. Ion trap (ITD) mass spectrometers cost significantly less than conventional HRMS and MS/MS instruments, are much simpler, require much less training and maintenance and are considerably cheaper to operate. The ITD has the capability of operating in advanced modes such as MS/MS, negative chemical ionization (NICI) and HRMS.

The capabilities and performance characteristics of the GC/ITD system will be evaluated by way of developing routine analytical methods for designated target compounds in various environmental matrices. The four groups of compounds designated for study include polynuclear aromatic hydrocarbons (PAH), toxaphene, polychlorinated biphenyls (PCBs) and chlorinated diphenyl ethers (CDPEs).

Results

Instrument sensitivity checks were done using standard autotune conditions. Full scan extracted ion chromatograms exhibited signal-to-noise (S/N) ratios of at least 5:1 for 5pg of the individual PAH. Pseudo-SIM scan extracted ion chromatograms gave slightly better S/N ratios. Nominal S/N ratio improvement occurred when using MS/MS functions. This is to be expected since the S/N work was done using standards. The true benefits of using MS and MS/MS compared to conventional GC detectors will be shown when analyzing real-matrix environmental samples, as both modes of mass spectrometer operation are selective enough to greatly reduce chemical interferences, thereby maintaining S/N ratios similar to those observed when analyzing standards.

Instrument performance was consistent at all PAH standard levels tested (10pg/uL to 1000pg/uL), yielding quantification accuracies of 96% - 110% with RSDs of 4% - 8%. PAH calibration curves, generated for injections up to 1000pg, most closely matched quadratic functions, especially for late eluting PAH such as benzo(g,h,i,)perylene. However, even using linear functions correlation coefficients still exceeded 0.996.

PAH ion ratios in the pseudo-SIM mode of operation were not classical as "M-2H" ions were almost equivalent in intensity to "M" ions (PAH quadrupole profiles usually have "M-2H" at 10% to 30% of "M"). During the isolation of the "M-2H" ion of the individual PAH the waveform amplitude used to resonantly eject the "M" ion was sufficiently large to not only cause ejection of the "M" ion but also cause its

fragmentation to the "M-2H" ion. This collisionally induced dissociation (CID) phenomenon was reproducible and could be used to increase instrument response to the "M-2H" ion (increased M-2H/M ratios), which allowed lower instrument detection limits and ion confirmation.

A routine, trace-level, solid phase extraction gas chromatography-mass spectrometry (SPE-GC/MS) method was developed to test for 17 target PAH in surface waters, drinking waters and groundwaters. The wet chemical preparation procedure consists of sample acidification, surrogate addition, sample aspiration through C₁₈ SPE cartridges, toluene elution and extract evaporation. After the addition of an internal standard, GC/MS analysis is complete. Compound separations are done by a DB-5ms fused silica capillary column in 35 minutes. Target compound identification (retention time plus target ions), quantification (parent ion + qualifying ion) and confirmation (ion ratios) at low ng/L (ppt) levels is accomplished by the ion trap mass spectrometer in the positive electron ionization (EI) pseudo-SIM mode.

Current Status

GC/ITD instrument performance has been established in EI MS mode of operation. A trace level solid phase extraction gas chromatography - ion trap mass spectrometer (SPE-GC/ITD) method has been developed for the testing of 17 PAH in drinking waters, surface waters and groundwaters. The SPE-GC/ITD PAH method uses labelled surrogates and internal standards to monitor method performance and has method detection limits (MDL) of approximately 1 ng/L (ppt). Lower method detection limits are possible by further optimizing the wet chemical preparation and GC/ITD parameters. A paper is being prepared for presentation at the 45th Annual (1997) American Society for Mass Spectrometry (ASMS) Conference.

Developing a trace level toxaphene analytical method applicable to water, soil/sediment, vegetation and biota is next on the agenda. The MS/MS and NICI capabilities of the GC/ITD system will be investigated while developing the toxaphene method.

Publications and Presentations

Trace Level Analysis of PAH in Drinking Waters by Gas Chromatography / Ion Trap Mass Spectrometry, Jeffry Plomley and Patrick Crozier, "Testing the Environment", IAETAL 9th Annual Conference, September 7-10, 1996, Toronto, Ontario, Canada.

Methods Development

Introduction

Method Development continues to be the most important focus of R&D activities in the Laboratory Services Branch. Only one in ten of the 1996 projects described in this section was generated internally. The other nine projects listed were started as a direct result of requests from LSB customers in the Waste Reduction Branch, Science and Technology Branch, Environmental Monitoring and Reporting Branch, and the West Central Region. Projects were almost evenly divided between organic analytes (6) and inorganic (4). Many other method development enhancements were introduced, but only those projects which required significant changes to the method description, or a completely new method write-up, are described here.

The new methods are being developed to support Ontario environmental regulations and guidelines (hazardous waste disposal, compost guidelines, contaminated sites, MISA) and programs (fish contaminants, DWSP). Two of the studies (iodine and dichloriodomethane in drinking water) were initiated to support a Ministry investigation to clean pipes in water distribution systems - replacement of such pipes has been estimated to be a \$600 million/year cost to Ontario residents. Without reliable analysis methods, it would not be possible to assess the possible environmental and human health impacts of such initiatives.

I. Hexane Micro-extraction Roller Methodology

| | |
|---------------|------------------------------------|
| Study Leader: | Eva Duchoslav |
| Study Team: | Jadwiga Mazur, Patrick Crozier |
| Customer: | All Drinking/Surface Water Clients |

Objectives

To develop a microextraction method for the trace level testing of chlorinated organic pesticides and PCBs in drinking waters, surface waters and groundwaters which will provide high quality data with increased analytical capacity and a reduction in the use of hazardous extraction solvents.

Background

Solvent microextraction techniques offer several advantages over traditional liquid/liquid extraction methods. The reduction in the use of solvents cuts down the amount of hazardous wastes produced as well as reagent costs. Microextraction techniques significantly reduce the source of analyte loss and experimental error by reducing the need for sample clean-up and solvent reduction after extraction. The sample preparation time can be reduced from days to hours. Extraction is carried out in the original sample container which removes the need for glassware preparation. Therefore, the use of microextraction techniques has the potential to save chemical reagents, labour and time and reduce costs. Solvent microextraction has been applied to the analysis of pesticides by the USEPA, but their Method 505 does not encompass the target pesticides and meet detection limits required by current MOEE/LSB methods. The modification of USEPA Method 505 to reach ng/L (ppt) detection limits for all organochlorine target compounds in MOEE/LSB Method OWOC-E3120B was initiated.

Results

A routine hexane microextraction roller method has been developed to test for 35 chlorinated organic target compounds. The wet chemical preparation procedure, which is done in the original 1-L amber sample bottle, consists of surrogate and hexane (2 mL) addition to the 800 mL sample followed by sample rolling for 90 minutes and direct extract transfer to an autosampler vial. Instrumental analysis is done by dual fused

silica capillary column GC - electron capture detection (GC/ECD) using internal standard quantification techniques. Compound separations are done on 30 metre DB-1 and DB-1701 columns using a 55 minute single ramp oven program. Target compounds must be detected on both analytical columns and be within a specified quantification tolerance to be considered present in the extract.

Method recoveries for individual target compounds in fortified waters (reagent and real matrix) were between 76% and 108% with RSDs generally better than 10% (see Table). Quality control data have shown the microextraction method to yield low recoveries of PCBs in naturally contaminated environmental samples. In general terms, the higher the degree of congener chlorination the lower the method recovery. At this time, the method is not recommended for quantitative reporting of PCBs results.

| OCs Microextraction Method - Instrument and Method Performance Summary | | | | | | | | |
|--|------------------------|---|------------|---------|--|----|--------------|---------|
| Compound | Instrument Performance | | | | Method Performance (fortified reagent water) | | | |
| | Standard (ng/mL) | N | Result (%) | RSD (%) | Spike (ng/L) | N | Recovery (%) | RSD (%) |
| hexachloroethane | 10 | 8 | 101 | 0.5 | 25 | 25 | 90 | 4 |
| 1,3,5-trichlorobenzene | 50 | 8 | 100 | 1.6 | 125 | 39 | 97 | 5 |
| 1,2,4-trichlorobenzene | 50 | 8 | 102 | 0.7 | 125 | 25 | 99 | 5 |
| 1,2,3-trichlorobenzene | 50 | 8 | 99 | 1.2 | 125 | 25 | 101 | 3 |
| hexachloro-1,3-butadiene | 10 | 8 | 100 | 1.5 | 25 | 39 | 76 | 6 |
| 2,4,5-trichlorotoluene | 50 | 8 | 99 | 1.3 | 125 | 39 | 99 | 5 |
| 2,3,6-trichlorotoluene | 50 | 8 | 100 | 2.0 | 125 | 25 | 100 | 4 |
| 1,2,3,5-tetrachlorobenzene | 10 | 8 | 101 | 0.8 | 25 | 25 | 102 | 3 |
| 1,2,4,5-tetrachlorobenzene | 10 | 8 | 101 | 1.3 | 25 | 39 | 103 | 6 |
| 1,2,3,4-tetrachlorobenzene | 10 | 8 | 100 | 2.4 | 25 | 39 | 106 | 6 |
| α ,2,6-trichlorotoluene | 50 | 8 | 100 | 0.3 | 125 | 25 | 101 | 2 |
| pentachlorobenzene | 10 | 8 | 100 | 0.4 | 25 | 25 | 93 | 4 |
| hexachlorobenzene | 10 | 8 | 100 | 1.5 | 25 | 39 | 95 | 6 |
| heptachlor | 10 | 8 | 102 | 0.7 | 25 | 25 | 92 | 7 |
| aldrin | 10 | 8 | 100 | 0.9 | 25 | 39 | 82 | 11 |
| p,p'-DDE | 50 | 8 | 100 | 0.9 | 125 | 39 | 86 | 11 |
| α -BHC | 10 | 8 | 100 | 0.7 | 25 | 25 | 96 | 11 |
| trifluralin | 50 | 8 | 100 | 0.9 | 125 | 25 | 92 | 7 |
| γ -BHC (lindane) | 10 | 8 | 100 | 1.0 | 25 | 39 | 96 | 9 |
| α -chlordane | 20 | 8 | 100 | 0.9 | 50 | 25 | 94 | 7 |
| γ -chlordane | 20 | 8 | 100 | 0.8 | 50 | 25 | 94 | 7 |
| oxychlordane | 20 | 8 | 101 | 0.7 | 50 | 25 | 95 | 6 |

| | | | | | | | | |
|----------------------------|-----|---|-----|-----|-----|----|-----|----|
| o,p'-DDT | 50 | 8 | 102 | 1.2 | 125 | 25 | 91 | 9 |
| p,p'-DDD | 50 | 8 | 100 | 0.9 | 125 | 39 | 96 | 8 |
| p,p'-DDT | 50 | 8 | 101 | 0.9 | 125 | 39 | 85 | 13 |
| methoxychlor | 50 | 8 | 103 | 2.0 | 125 | 25 | 104 | 4 |
| heptachlor epoxide | 10 | 8 | 100 | 1.0 | 25 | 39 | 106 | 4 |
| endosulfan I | 20 | 8 | 100 | 1.1 | 50 | 39 | 104 | 4 |
| dieldrin | 20 | 8 | 101 | 1.2 | 50 | 25 | 104 | 3 |
| endrin | 40 | 8 | 99 | 1.7 | 100 | 39 | 108 | 4 |
| endosulfan II | 40 | 8 | 100 | 1.3 | 100 | 25 | 105 | 5 |
| endosulfan cyclic sulphate | 40 | 8 | 101 | 1.1 | 100 | 39 | 104 | 6 |
| mirex | 50 | 8 | 101 | 1.4 | 125 | 25 | 94 | 8 |
| octachlorostyrene | 10 | 8 | 100 | 1.8 | 25 | 39 | 80 | 8 |
| polychlorinated biphenyls | 100 | 8 | 105 | 4.5 | 100 | 16 | 93 | 11 |
| toxaphene | 100 | 8 | 101 | 7.5 | 250 | 16 | 105 | 14 |

Current Status

Method development is basically complete. The method (LSB LIMS Method # E3400A) is being internally audited before being put on line for routine sample testing. The microextraction method has been validated against the LSB dichloromethane liquid/liquid extraction method using real-matrix spiked samples, NIST reference materials and CAEAL audit samples. The method is currently under going CAEAL accreditation. Some further method development is required to improve PCBs results either through improved extraction efficiency or use of surrogates for PCB congener recovery correction.

Publications and Presentations

1. The Determination of Organochlorine Pesticides (OCs) and Other Chlorinated Organic Compounds in Water by Hexane Microextraction and Gas Chromatography - Electron Capture Detection (GC/ECD), MOEE/LSB LIMS Method # E3400A, Drinking Water Analyses Section.
2. Comparison of Different Extraction Techniques for the Determination of Organochlorine Compounds in Water, Eva Duchoslav, 28th Eastern Canada Pesticides and Environmental Contaminants Workshop, May 27-29, 1996, Guelph, Ontario, Canada.

II. Addition of Dioxin-like PCBs to Dioxin/Furan Analysis

| | |
|---------------|----------------------------------|
| Study Leader: | Dave Waddell |
| Study Team: | Karen MacPherson, Terry Kolic |
| Customer: | All Clients of Dioxin/Furan Unit |

Objective

To develop a modified dioxin/furan analytical method that could also be used for the determination of the 13 "toxic" PCBs in the same analytical run.

Background

The selective bioaccumulation of PCBs and weathering of technical PCB mixtures has dictated the development of congener specific methods for analytical PCB determination. Thirteen of the 209 possible PCBs exhibit dioxin-like toxicity, and interest in these PCBs increased after the development of 2,3,7,8-tetrachlorodibenzo-p-dioxin Toxicity Equivalency Factors (TEFs) for them (see Table I). The determination of these dioxin-like PCBs is challenging because the data quality objectives are as rigorous as those needed to determine the chlorinated dioxins and furans.

High Resolution Mass Spectrometry, approximately 2 orders of magnitude more sensitive than GC/MS or GC/ECD and Isotope Dilution Quantitation are needed to meet strict data quality objectives (i.e. sensitivity, selectivity, precision & accuracy) required for dioxin-like PCB analysis. A complete set of standards has not been available until recently and this has limited method validation. The elution order of PCB congener groups overlap significantly on a DB-5 (SE-54) capillary column and makes chromatographic separation and detection more difficult than for PCDD/PCDF analysis.

Results

Initial reports in the literature indicated that five of the "toxic 13" PCB congeners (PCBs #77, #105, #118, #126 and #169) could be analyzed using a standard dioxin/furan isotope dilution method. This was not found to be the case, and extensive modifications to the standard LSB dioxin/furan method were required to analyze these

five PCB congeners at the same time as the dioxins/furans. However, the remaining eight dioxin-like congeners could also be determined by using the modified method without further modifications.

Instrument experimental conditions have been optimized separately for the PCB and dioxin/furan analyses. Optimization of chromatographic conditions to enable concurrent acquisition of PCBs and PCDD/Fs is being carried out. The co-elution of PCB congeners with different levels of chlorination may require that some PCB congeners be determined in a separate chromatographic run. Experiments to determine chromatographic conditions required for the isolation of the initial five congeners in sample extracts have been completed. Modifications of cleanup procedures needed for the remaining eight congeners are still under investigation.

Current Status

Instrumental conditions for the GC/MS determination of a set of up to 46 PCB congeners have been determined and are being optimized with respect to interferences and potential false positives. Depending on final instrumental conditions and client needs a list of PCB congeners greater than 13 may be possible. Optimization of open column chromatography for the 13 dioxin-like PCB congeners is underway.

TABLE I

| TYPE | CONGENER | | TEF |
|------------|-----------|-----------------------|---------|
| | IUPAC NO. | CHLORINE SUBSTITUTION | WHO/PCS |
| NON-ORTHO | 77 | 3,3',4,4' | 0.0005 |
| | 126 | 3,3',4,4',5 | 0.1 |
| | 169 | 3,3',4,4',5,5' | 0.01 |
| MONO-ORTHO | 105 | 2,3,3',4,4' | 0.0001 |
| | 114 | 2,3,4,4',5 | 0.0005 |
| | 118 | 2,3',4,4',5 | 0.0001 |
| | 123 | 2',3,4,4',5 | 0.0001 |
| | 156 | 2,3,3',4,4',5 | 0.0005 |
| | 157 | 2,3,3',4,4',5' | 0.0005 |

| | | | |
|----------|-----|------------------|---------|
| DI-ORTHO | 167 | 2,3',4,4',5,5' | 0.00001 |
| | 189 | 2,3,3',4,4',5,5' | 0.0001 |
| | 170 | 2,2',3,3',4,4',5 | 0.0001 |
| | 180 | 2,2',3,4,4',5,5' | 0.00001 |

III. Determination of Total Iodine in Drinking Water

| | |
|---------------|--|
| Study Leader: | Mark Powell |
| Study Team: | Ray McVicars |
| Customer: | Science and Technology Branch (Tony Edmonds) |

Objectives

To develop a method to measure the concentration of total iodine in treated drinking water.

Background

Water distribution systems (mains) have a limited life. Most systems become clogged with deposits made by bacterial action before corrosion has affected the mechanical integrity of the pipes. Maintenance of chlorine residuals and mechanical cleaning can help but in many cases this is either not possible or too late and pipe replacement becomes the only alternative. Many systems in Ontario are approaching the end of their useful life of 70 or more years. Replacement costs for Ontario are estimated at \$600,000,000 per year to keep pace with the need.

A potential technology, which has been used successfully elsewhere, is water mains cleaning by using chlorine/iodine disinfectant. Provided the iodine is at low enough concentrations so it does not present a significant hazard to anyone consuming the water, it appears to work effectively. This low iodine/chlorine cleaning process is to be piloted in Ontario at Port McNicoll this year and this will be the source of the samples for analysis. Should the cleaning process be effective there will be widespread future demand for total iodine analysis from many municipalities across Ontario.

Results

Total iodine in aqueous solutions (drinking water) can be determined by ICP-MS as I^+ which will be a proportional representation of I_2 . Iodine is a halogen and will produce mostly negative ions upon ionization. However, some positive ions are produced which can be measured by our mass spectrometer. Although a smaller number of positive ions are produced, this will not adversely affect the detection limits achievable by using ICP/MS.

The ion source completely ionizes the atoms and molecules, and hence, total iodine will be measured. It does not matter which form or valence state iodine is in originally (iodide or iodate), as long as there is minimal particulate in the sample. Excessive particulate may give rise to adsorption or complexing of iodine onto the surface of the particulate and cause a bias in the true concentration measurements. Detection limits, precision, accuracy and potential interferences are in the process of being determined.

Current Status

A method has been developed for the analysis of total iodine in drinking water. The detection capability of this technique reaches close to 50 ppt iodine. The short term precision of iodine measurements are 5% rsd and method precision is consistent from run to run.

Although the method precision is good, the accuracy is unknown because reference materials are not available. However, as the customer has emphasized reproducibility as being of principal importance, the method is adequate as-is for its intended use (the production of semi-quantitative data).

Field studies on sample stability have produced excellent results using sodium thiosulphate as a preservative (1% concentration). Studies have shown minimal iodine loss with preservative added over a 60-day period. The use of the direct injection nebulizer (DIN) enhances instrument performance while minimizing washout time with greater concentrations of iodine.

IV. Determination of Dichloriodomethane in Water

| | |
|---------------|--|
| Study Leader: | Robert Salemi |
| Study Team: | Michael Tjepkema |
| Customer: | Science & Technology Branch (Tony Edmonds) |

Objective

To develop a method for the trace determination of dichloriodomethane (DCIM) in treated water.

Background

The previous project in this Report (Determination of Total Iodine in Drinking Water) describes the use of chlorine/iodine as a disinfectant to clean pipes (in water distribution systems) to reduce their rates of deterioration, and therefore reduce the costs of repair. In addition to the need to monitor total iodine, a method was needed to monitor dichloriodomethane, which may be formed during the disinfection process, much as trichloromethane is produced during the chlorination of drinking water.

Results

Dichloriodomethane (DCIM) is not commercially available. Therefore, a synthetic pathway utilizing chloroform and sodium iodide was developed by Dr. Michael Tjepkema. Purification of the material via fractional distillation provided a material of sufficient purity to be used for quantitative method development purposes. DCIM was found to behave in a similar manner to the other trihalomethanes (THMs). Therefore, it was decided to simply extend the existing THM method to DCIM determination. Performance evaluation of the THM method for DCIM provided satisfactory results, with a minimum detection limit of $0.2 \mu\text{g/L}$, and precision of $<3\%$ rsd throughout the required range of operation of the method (up to $10 \mu\text{g/L}$).

Current Status

An LSB method with the THMs and DCIM in the parameter list has been adopted, for clients conducting iodine rehabilitation treatment of water treatment plants and water distribution systems.

V. Development of Alternative Methods for Testing Hazardous Waste Leachate

| | |
|---------------|---------------------------|
| Study Leader: | Heng Jin |
| Study Team: | Yvonne Jones, Rusty Moody |
| Customer: | Waste Reduction Branch |

Objectives

To develop a rapid, rugged, accurate and precise leach test for organics in hazardous waste; to be used in support of Regulation 347.

Background

The Ontario Regulation 347 leachate extraction procedure was developed for inorganic analytes and some pesticides. The need to develop land disposal restrictions for hazardous wastes and to expand the list of leachate toxic chemicals required a leach test that is applicable to a wide range of organic chemicals, including volatiles. The USEPA has developed such a method, which employs a zero head space extractor to prevent the loss of volatile organics.

Results

The USEPA Toxicity Characteristic Leachate Procedure (TCLP) was investigated for the analysis of volatile organics. The instrumental, analytical conditions were determined, and the standard curves were established. The recoveries of 32 analytes (spiked leachate solution), which were taken through the entire extraction procedure, ranged from 82% to 120% when analysed immediately after extraction. Recovery losses reached 40% when the extracts were allowed to sit for 3 days prior to analysis.

Analytical conditions for semi-volatile and non-volatile parameters have been determined and the standard calibration curves were established. Twenty-seven neutral and basic compounds and nine acidic polar compounds were studied. Recoveries of the neutral and basic compounds in the spiked solutions generally exceeded 80%.

Current Status

Recoveries of the base/neutral and acidic compounds must be determined for spikes taken through the entire extraction process. Also, recoveries of all the parameters studied must be determined for spikes of clean sand and solid waste samples which then undergo the entire extraction and analytical process.

VI. Development of a Leachate Extraction Procedure for Fluorescent Bulbs

| | |
|---------------|------------------------|
| Study Leader: | Rusty Moody |
| Study Team: | Ray Leger |
| Customer: | Waste Reduction Branch |

Objective

To develop an accurate and precise leach test for fluorescent light bulbs; to be used in support of Regulation 347.

Background

The move to more energy efficient lighting sources has led to the greater use of fluorescent bulbs. These bulbs each contain from 10 to 20+ mg of mercury, and thousands of mercury containing bulbs are disposed in landfills. Current leachate procedures in Canada and the US yield inconsistent results for mercury due to sample variations due to the manufacturer of the bulb, the bulb's age, and the loss of mercury during the leachate and analysis procedure. Work in the USA has suggested the analysis of whole bulbs should be performed, rather than analysis of a 50-100 g aliquot. This project was started at Ontario Hydro Technologies (OHT), with the support of the bulb manufacturers. One manufacturer provided bulbs from the same production run and with the same number of hours of use, so bulb variability was eliminated as much as possible. A second manufacturer provided new bulbs from a single production run. Initially OHT performed the mercury analyses and MOEE-LSB staff performed the analyses of the other metals covered in Regulation 347. MOEE staff completed the project.

Results

Ontario Hydro Technologies designed and constructed a whole bulb extractor, a 143 cm x 11.4 cm polypropylene bottle capable of holding an unbroken 4' bulb. Initial results using this whole bulb container and a modified USEPA leachate procedure showed that mercury recoveries were far more consistent using this proposed method than with the current Regulation 347 method. MOEE results showed a 13 fold increase in mercury recovery for the proposed method using one type of bulb and a 7 fold increase using the other type of bulb. The mercury losses in the current Regulation 347 method may be attributable to loss of mercury vapour and dust during bulb breaking and weighing and vapour loss during pH adjustment. The USEPA method eliminates losses during extraction since there are no pH adjustments made. Losses during breakage and weighing can be limited by breaking the bulbs in plastic bags, mixing thoroughly while the bulb is still in the bags, and weighing quickly.

Current Status

Experimental work is finished. The final report and method need to be written and submitted to the Waste Reduction Branch. If accepted, this method would be classified as an alternative procedure under Regulation 347. The proposed method is quite different from the current leachate procedure. Private sector laboratories may not wish to use specialized, dedicated extractor vessels for these samples. If this is the case, more work will have to be done to improve recoveries using smaller amounts of bulb during the extraction.

VII. Determination of Metals in Compost Material

| | |
|---------------|---|
| Study Leader: | Liz Pastorek |
| Study Team: | Dan Toner, Liz Pastorek, Jane Thrush, Esa Mistry, Phil Choo |
| Customer: | Waste Reduction Branch |

Objective

To develop a Performance Based Method System (PBMS) to be applied to the development of methods capable of producing data that will meet or exceed Data

Quality Objectives (DQO's) as outlined in the MOEE document "Guideline for the Production and Use of Aerobic Compost in Ontario"; to develop a MOEE method for the Analysis of Metals in Compost.

Background

MOEE-LSB was asked to assist the Waste Reduction Branch in evaluating existing methods (or developing new ones) for the implementation of MOEE Compost Guidelines. Previously, Vegetation/Soil/Sediment methods have been applied to compost-like material, but no compost method was established. These methods, which consisted of a strong mixed acid extraction followed by ICP analysis, along with the EPA Solids Digestion method (EPA 3050A), were applied to various reference materials, (no Compost reference material exists at present), and Compost composite samples. It was found that all of these methods could meet the DQO's. Initial sample treatment (drying, grinding, sieving) was also studied.

Results

1. Data Quality Objectives were established based on analysis of Reference Materials. These included MDL's, precision limits, and recovery limits. A precision of 10% RSD, and accuracy of $100 \pm 10\%$ was determined.
2. A method based on the MOEE Soil Metals Analysis method was established for Compost (E 3394A).
3. The study of the initial sample treatment, indicated that the entire sample should be sieved to < 4.75 mm (#4 sieve) after air drying, gentle disaggregation, and removal of non-compostable components (> 1 mm). In order to include all the analytes, the processing of choice would be grinding or sieving sub-samples to particle size < 2.0 mm. These sub-samples should be between 20 and 200 g in size.

Current Status

The Data Quality Objectives have been added to the Guidelines, and a MOEE-LSB compost method has been developed and approved. Presentations of the work have been made at the Composting Council of Canada's Sixth Annual Conference.

VIII. Determination of Polychlorinated Biphenyls in Compost

| | |
|---------------|---|
| Study Leader: | Rob Brunato |
| Study Team: | Dan Toner, Liz Pastorek, Tony Chen, Jane Thrush |
| Customer: | Waste Reduction Branch |

Objective

To develop a new method for the analysis of PCBs in compost for the implementation of MOEE compost guidelines.

Background

Two extraction techniques were evaluated for this study: supercritical fluid extraction (SFE) using carbon dioxide and water as the extraction solvent, and robotic extraction using 25% dichloromethane in hexane as the extraction solvent.

Results

Robotic Extraction. PCBs were extracted twice from a 5g compost sample using a 25% dichloromethane/hexane mix. The combined extract was then filtered through anhydrous sodium sulphate and made up to 100mL in a volumetric flask. A 20 mL aliquot was reduced in volume to 1 mL for clean-up on a 24 cm pre-conditioned 100-200 mesh Florisil column. PCBs were eluted by using 25-30 mL hexane. Compost extracts were then reduced in volume to 5 mL and analyzed by GC/ECD. PCB results from 10 replicates spiked with PCB standards had an overall recovery of 111% (s.d. 8%).

Supercritical fluid extraction. PCBs were extracted from compost samples using carbon dioxide modified with water. One gram compost samples containing 500 μ L water were extracted using a HP 7680A supercritical fluid extractor. Extractions were performed at 100°C with carbon dioxide at 5000 psi. Extraction times were 1 minute (static) or 20 minutes (dynamic). During the extraction the Octadecylsilane trap was maintained at 15°C. After extraction, the trap was heated to 40°C before analytes were eluted from the Florisil column with 10 mL hexane. This fraction was evaporated to 5 mL and analyzed by GC/ECD. Results from 10 replicates spiked with PCB

standards showed an overall recovery of 107% (s.d. 5%).

Current Status

Advantages of the SFE method for PCBs in compost include: improved reproducibility, better precision, 90% reduction in solvent use, elimination of the use of chlorinated solvents, and a reduction in sample extraction and cleanup time. The SFE method was therefore adopted. It has been audited and is now an official MOEE-LSB method.

IX. Determination of Petroleum Contamination in a Soil Matrix

| | |
|---------------|------------------------------|
| Study Leader: | David Morse |
| Study Team: | David Morse |
| Customer: | Standards Development Branch |

Objective

To develop a method to analyze a soil or sediment sample for petroleum contamination, which will provide both quantitative results and product identification.

Background

Petroleum hydrocarbon analysis has been performed by numerous techniques, primarily for the decommissioning of contaminated sites. MOEE-LSB, to support the procedures described in the MOEE report *Guidance on Sampling and Analytical Methods for Use at Contaminated Sites*, has developed a technique to rapidly screen samples for petroleum hydrocarbons by using a combination of headspace GC and microwave solvent extraction, followed by a combination of GC and gravimetric analysis. A similar technique has also been developed that will allow identification of the type of petroleum contamination over the carbon range C5 - C50, for application primarily in the investigation of spills. This technique also uses a combination of headspace GC and microwave solvent extraction, but is followed by high temperature GC analysis.

Results

Determination of Petroleum Hydrocarbons in Soil for the Decommissioning of Contaminated Sites. Hydrocarbons are determined according to their boiling range, which is divided approximately into Light (C5 to C24) and Heavy (C17 and greater) fractions. The light fraction can be further divided into total purgeable hydrocarbons (C5 to C10), and extractables (C10+ to C24). Total purgeables are determined by headspace GC, and extractables by microwave solvent extraction using 1:1 acetone:hexane, followed by back-extraction, silica separation, and GC. The Light fraction recovery is about 90%, with a method detection limit of 10 mg/Kg (ppm). The Heavy fraction is extracted by the same technique as the "extractable" portion of the Light fraction, but is quantified by gravimetry. Recoveries for the Heavy fraction are about 90%, with method detection limit of 100 ppm. A 15-minute microwave solvent extraction with acetone:hexane gives comparable results to a 24 hour Soxhlet extraction using either dichloromethane or acetone:hexane for both the extractable portion of the Light fraction and for the Heavy fraction.

Determination of Total Petroleum Hydrocarbons (C5 to C50) in Soil. For this method, Total Petroleum Hydrocarbons (TPH) are defined as all petroleum hydrocarbons from n-pentane (C5) to n-pentacontane (C50). The full hydrocarbon range is divided into three sub-fractions: Light (C5-C10; i.e. gasoline, naphtha), Medium (C10-C24; i.e. diesel, jet fuel, home heating fuel), and Heavy (C24-C50; i.e. lubricating oil). TPH is analyzed using similar methods as described previously for the Light fraction, but the extractable range is extended to pentacontane by the use of high temperature GC. Recoveries for the entire range of TPH are about 85%, with method detection limit of 20ppm. This method will also allow for the identification of the petroleum product found, throughout the C5-C50 carbon range.

Current Status

Both the methods described above are complete, and are in routine use. Future work is planned to apply these techniques to the analysis of aqueous sample types.

X. Determination of Aniline, Benzothiazole, Mercaptobenzothiazole, and Carboxin in Water by Isotope Dilution GC/MS

| | |
|----------------|-------------------------------|
| Study Leader : | Rocsana Lega |
| Study Team : | Michael Tjepkema, Otto Meresz |
| Customer : | West Central Region |

Objective

To develop a reliable method for the determination of analytes on the EMMPL list, to be adopted as the routine procedure for use in the Wastewater Unit.

Background

Benzothiazole compounds have been widely used as rubber vulcanization accelerators, antioxidants, corrosion inhibitors, and heat stabilizers. Therefore, benzothiazole and its derivatives have been detected in such environmental samples as waste water, ground water, river water, tap water, landfill leachates, atmospheric deposition, coastal sediments, and fish. Few reports on the extraction and analysis of benzothiazole derivatives in aqueous media have been published. Aniline is another substance found in the environment for which limited information exists. Because of its physical and chemical properties (relatively volatile, basic, prone to degradation under some conditions), the determination of aniline requires special considerations. Because of ongoing monitoring at certain contaminated industrial sites in Ontario, it was necessary to develop reliable analytical methods for these contaminants.

Results

Difficulties were encountered with the instrumental detection of mercaptobenzothiazole (MBT) in a standard, because of adsorption and/or degradation in the GC/MS system employed for this work. By replacing the splitless GC injector by a SPI on-column injector, the MBT could be detected, but considerable tailing of its GC peak was observed. Treatment with diazomethane yielded two methylated isomers which were easily quantified.

A suitable extraction procedure was then developed. MBT was effectively

recovered from spiked distilled water samples, but not from spiked drinking water, likely from residual chlorine which promotes oxidation of the MBT. Experiments were done to identify the oxidation products and to reverse the reaction. Reduction experiments carried out by using zinc/acetic acid, and with sodium borohydride, produced benzothiazole (BT) and some MBT. Unfortunately, BT is a target analyte in this method, and is widely present in environmental samples.

The extra methylation step introduced for the determination of MBT lowered the recovery of other target compounds, notably the carboxin. To deal with the erratic recoveries obtained, an isotope dilution technique was used, in which the concentrations of analytes were recovery-corrected, according to the recoveries of deuterium-labelled surrogates. Deuterated aniline was available commercially, and deuterated analogues of the other analytes were synthesized at LSB by Dr. Michael Tjepkema. By using the isotope dilution method, the precision of the determinations improved dramatically.

Current Status

Method detection limits, recoveries, and other method attributes were determined for the target analytes, and the completed method documentation prepared for review by the Quality Management office. Some real-matrix samples are being analyzed to test the performance and range of applicability of the method.

Publications and Presentations - 1996

Analytical Laboratory Services

A. Publications

1. Jennifer L. Mueller, Ijaz Ahmad, and Martin S. Gibson. 3,4-Methylenedioxy-2-phenylpyrrolo[4, 3, 2-ij]isoquinoline: an Unusual Synthesis of this Heterocyclic System. *J. Chem. Res.* **1995**, 3024.
2. Sylvia Cussion and Sathi Selliah. *Interlaboratory Study 96-1: Total Alkalinity, Cations, Anions, and Trace Elements in Water*. Ontario Ministry of Environment & Energy, Laboratory Services Branch Report, July 12, 1996.
3. Sylvia Cussion and Air Quality Research Branch, Atmospheric Environment Service. *Interlaboratory Study 94-1, Part A: Trace Metals Spiked Into Precipitation; Part B: Trace Metals Spiked Onto Filters*. Ontario Ministry of Environment & Energy, Laboratory Services Branch and Environment Canada Report (ISBN 0-7778-4660-8), December, 1996.
4. Sylvia Cussion. *Interlaboratory Study 93-4: Polycyclic Aromatic Hydrocarbons (PAH)*. Atmospheric Environment Service, Environment Canada and Ontario Ministry of Environment & Energy, Laboratory Services Branch Report (ISBN 0-7778-3392-1), May, 1996.
5. Jeffry B. Plomley, Raymond E. March, and Roger S. Mercer. Tandem Mass Spectrometry of Polychlorodibenzo-p-Dioxin and Polychlorodibenzofuran in a Quadrupole Ion Trap. 1. Comparison of Single-Frequency, Secular Frequency Modulation, and Multifrequency Resonant Excitation Modes. *Anal. Chem.* **1996**, 68(14), 2345-52.
6. R.M. Hoff, M.M.J. Strachan, C.W. Sweet, C.H. Chan, M. Shackleton, T.F. Bidleman, K.A. Brice, D.A. Burniston, S. Cussion, D.F. Gatz, K. Harlin, and W.H. Schroeder. Atmospheric Deposition of Toxic Chemicals to the Great Lakes: A Review of Data through 1994. *Atmos. Environ.* **1996**, 30(20), 3505.
7. Mark Stelmacovich, Anton Mahne, and Ray Clement. Three Views of High School Co-operative Education: The School, The Student, The Employer. *The Crucible* **1996**, 27(5), 12-15.
8. EnviroAnalysis: *Practical Methods for Environmental Analysis*; edited by Robert Burk and Ray E. Clement. Proceedings of the EnviroAnalysis Conference, Ottawa, ON May 13-16, 1996. Polyscience Publishers: Morin Heights, Canada

(ISBN 0-921317-62-X), 369 pp.

9. M. Sage, P. Hubber, O. Ting, R. Luniewski, L. Au, D. Toner, and P. Yang. "Development and Applications of a Multi-bed Adsorbent Cartridge Sampling, Thermal Desorption/Gas Chromatograph/Mass Spectrometry System for Airborne Volatile Organic Compounds Analysis", in *EnviroAnalysis: Practical Methods for Environmental Analysis*; R. Burk and R.E. Clement, eds. Polyscience Publishers: Morin Heights, Canada (ISBN 0-921317-62-X), 95-98.
10. Patrick W. Crozier. "Application of a Multidimensional Chromatographic/Mass Spectrometric Detection System to Trace Level Organics Analyses", in *EnviroAnalysis: Practical Methods for Environmental Analysis*; R. Burk and R.E. Clement, eds. Polyscience Publishers: Morin Heights, Canada (ISBN 0-921317-62-X), 197-201.
11. L. Au, B. Kanabe, R. Luniewski, L. Nasri, P. Hubber, D. Toner, and P. Yang. "Gas Chromatography/Isotope Dilution Mass Spectrometry Analysis of Airborne Benz[a]Pyrene Using ¹³C-labelled Benzo[a]pyrene and a Low Resolution Mass Spectrometer - Method Development and Evaluation", in *EnviroAnalysis: Practical Methods for Environmental Analysis*; R. Burk and R.E. Clement, eds. Polyscience Publishers: Morin Heights, Canada (ISBN 0-921317-62-X), 207-210.
12. David W. Boomer. "Performance-Based Methods", in *EnviroAnalysis: Practical Methods for Environmental Analysis*; R. Burk and R.E. Clement, eds. Polyscience Publishers: Morin Heights, Canada (ISBN 0-921317-62-X), 333-344.
13. George Crawford. "A Performance Based Methods System for Environmental Laboratories in Ontario", in *EnviroAnalysis: Practical Methods for Environmental Analysis*; R. Burk and R.E. Clement, eds. Polyscience Publishers: Morin Heights, Canada (ISBN 0-921317-62-X), 355-360.

B. Presentations

1. *R.E. Clement*, "A Role for Government in Environmental Laboratory Training", presented at *EnviroAnalysis'96* Conference, May 13, 1996, Ottawa, Ontario.
2. *R.E. Clement*, "The Role of Government and Industry in Environmental Education and Training", Invited Seminar presented at Mohawk College, May 8, 1996, Hamilton, Ontario.
3. *R.E. Clement*, "Science, Science Fiction, and Toxic Chemicals", Invited Seminar presented at OSEE Annual Conference, May 3, 1996, Bolton, Ontario.
4. *R.E. Clement*, "Environmental Analysis - Past, Present and Future", Invited Seminar presented to the Guelph Student Chapter, Air and Waste Management Association (Ontario Section), February 8, 1996, Guelph, Ontario.
5. *R.E. Clement*, "Environmental Careers", Invited Seminar presented at Monsignor Johnson High School, *Career Day*, February 2, 1996, Rexdale, Ontario.
6. *Ijaz Ahmad* and *Liz Pastorek*, "Developing a Performance Based Method Approach for the Analysis of Metals and PCBs in Compost Materials", presented at the 6th Annual Conference, Exhibition and General Meeting of the Composting Council of Canada, Toronto, November 6-9, 1996.
7. *Liz Pastorek*, "A Comparison of Methods for the Analysis of Metals in Compost", presented at 6th Annual Conference of the Composting Council of Canada, Toronto, Ontario November 7, 1996.
8. *Ijaz Ahmad*, "Data Quality Objectives for Analyzing Metals and PCBs in Compost Materials", presented at the MOEE Workshop on Analytical Methodologies for Compost, Toronto, November 6, 1996.
9. *George Crawford*, "Performance Based Method Systems", presented at the MOEE Workshop on Analytical Methodologies for Compost, Toronto, November 6, 1996.
10. *Liz Pastorek*, "Analysis of Metals in Compost", presented at the MOEE Workshop on Analytical Methodologies for Compost, Toronto, November 6, 1996.
11. *V.Y. Taguchi*, "Analytical Applications of Mass Spectrometry", Lecture presented to 3rd Year Chemistry Students, University of Western Ontario, February 1996.
12. *M. Sage*, *P. Hubber*, *O. Ting*, *R. Luniewski*, *L. Au*, *D. Toner*, and *P. Yang*. "Development and Applications of a Multi-bed Adsorbent Cartridge Sampling, Thermal Desorption/Gas Chromatograph/Mass Spectrometry System for Airborne

Volatile Organic Compounds Analysis", presented at *EnviroAnalysis'96*, Ottawa, Canada May 15, 1996.

13. *George Crawford*, "PBMS - What's the MOEE up to Now?", presented at *EnviroAnalysis'96*, Ottawa, Canada May 15, 1996.
14. *David Boomer*, "Performance Based Methods", presented at *EnviroAnalysis'96*, Ottawa, Canada May 15, 1996.
15. *Patrick Crozier*, "Application of a Multidimensional Chromatographic/Mass Spectrometric Detection System to Trace Level Organics Analyses", presented at *EnviroAnalysis'96*, Ottawa, Canada May 16, 1996.
16. *Lorna Grey*, "Determination of Organophosphorus Insecticides in Drinking Water and Raw Water by Solid Phase Extraction Followed by High Performance Liquid Chromatography", presented at 28th Eastern Canada Pesticides and Environmental Contaminants Workshop, Guelph, Ontario May 27-29, 1996.
17. *Eva Duchoslav*, "Comparison of Different Extraction Techniques for the Determination of Organochlorine Compounds in Water", presented at 28th Eastern Canada Pesticides and Environmental Contaminants Workshop, Guelph, Ontario May 27-29, 1996.
18. *Jeffrey Plomley* and *Patrick Crozier*, "Trace Level Analysis of PAH in Drinking Waters by Gas Chromatography/Ion Trap Mass Spectrometry", presented at 9th Annual Conference, International Association for Environmental Testing Laboratories, Toronto, Ontario September 7-10, 1996.
19. *Vince Taguchi*, *Steve Jenkins*, *Dave Wang*, *J.-P. Palmentier*, and *Don Robinson*, "Analysis of Geosmin and 2-Methylisoborneol by Isotope Dilution High Resolution Mass Spectrometry", presented at 44th ASMS Conference on Mass Spectrometry and Allied Topics, Portland, Oregon May 1996.
20. *Mark Powell*, "Quality Management Practices Relating to Spectroscopy Methods", presented at the Canadian Mineral Analysts Conference, Peterborough, Ontario July 1996.

